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FULLERENES OF THE ΔN=4 SERIES

Alexander I. Melker[1*], Tatiana V. Vorobyeva[2], Ruslan M. Zarafutdinov[1]

[1]Department of Mechanics and Control Processes, [2]Department of Experimental Physics

Peter the Great St. Petersburg Polytechnic University, Polytekhnicheskaya 29

195251, St. Petersburg, Russian Federation

*e-mail: newton@imop.spbstu.ru

Abstract. Fusion reactions of cages and fullerenes C_4, C_6 C_8, C_{10}, C_{12} and C_{14} with each other are modeled on the basis of Arrhenius's postulate. It means that at first there forms an intermediate compound and afterwards a chemical reaction is going on. During the reactions new covalent bonds between the reacting atoms of different fullerenes are formed and old covalent bonds are destroyed. The process is similar to fusion of bubbles in a soap solution. The graphs describing the process are suggested. We have obtained fullerenes C_8, C_{12} C_{16}, C_{20}, C_{24} and C_{28} that can be incorporated in the fullerene periodic system as the Δn=4 series.

Keywords: cage, energy, fullerene, fusion reaction, graph, modeling

1. Introduction

In Ref. [1, 2] we have suggested the periodic system of fullerenes. It consists of horizontal series and vertical columns (groups). The horizontal series form the Δn periodicities having one and the same main characteristic feature; the fullerene structure changes from threefold symmetry to sixfold through four and fivefold ones. The vertical columns include the fullerenes of one and the same symmetry, the mass difference Δm for each column being equal to a double degree of symmetry. We suppose that these features can be taken as a basis for rigorous fullerene classification. The Δn periodicities studied consist of the following series: Δn= 6, 8, 10, 12, 14, 16 and 18; they include fullerenes from C_{14} to C_{108}. The structure, energy and formation mechanism for the most of series is discussed elsewhere [3-5].

In addition to these series, we suppose that it is possible to incorporate into the system other series and columns. In this contribution we present fullerenes of the Δn=4 series fitted our classification, their structure, energy and possible formation mechanisms being given. We assume that the fullerenes of identical groups have similar properties.

2. Structure and energy

The Δn=4 series must contain the following perfect species: C_8, C_{12}, C_{16}, C_{20}, C_{24} and C_{28}. Adding to them fullerenes C_8 and C_{28}, we obtain the full series presented in Fig. 1. Here it is accepted that the symmetry of double bonds location about the major axis of fullerenes coincides with that of fullerene C_{60}. It should be emphasized that the fullerenes of large size, having only single bonds are unstable and highly distorted. The optimized structures and energies of the fullerenes shown are obtained through the use of Avogadro package [6], a modified geometric graphic being developed because the package graphic is incomprehensible. There are suggested several mechanisms of fullerene formation [3]. Consider those of them which can explain the formation of fullerenes shown in Fig. 1.

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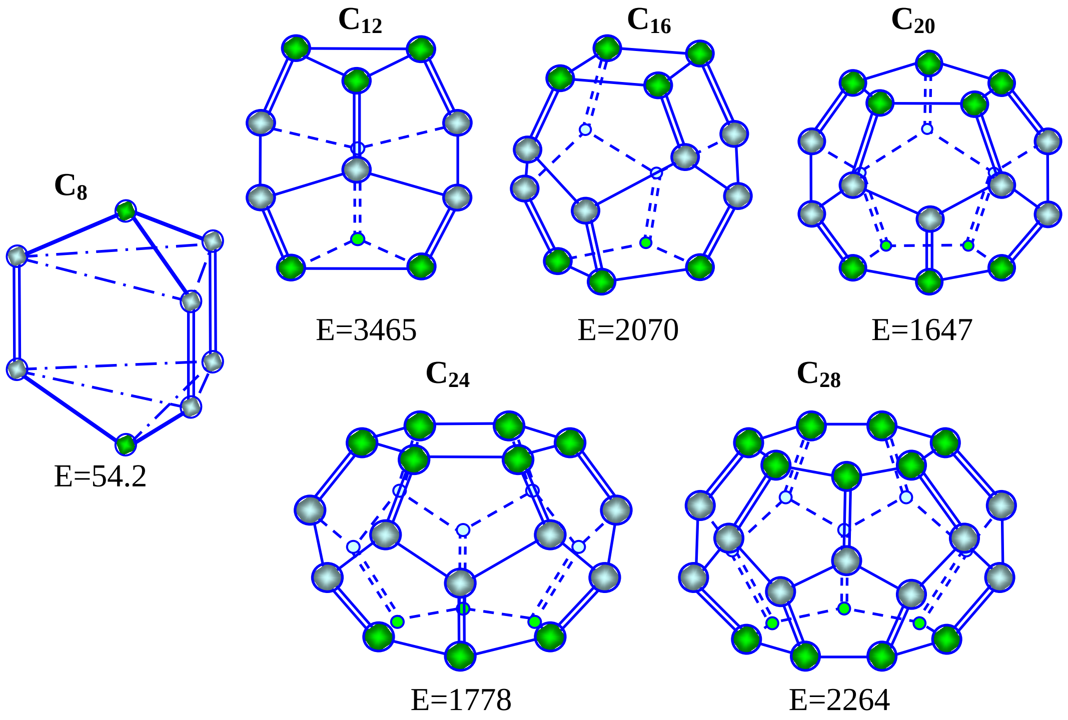

Fig. 1. Structure and energy (kJ/mol) of the Δn=4 series fullerenes

3. Fusion reactions of elementary fullerenes

Fullerenes can be imagined to grow in particular by reacting with each other, similar to bubbles in a soap solution. Our group pioneered in suggesting and applying this mechanism to cupola half fullerenes and obtained fullerenes of the Δn=8 series [3]. A little later we have considered reactions of elementary fullerenes (from C_4 to C_{12}) with each other as well as with their heirs. Under the elementary fullerenes we understood a tetrahedron, a cube, and triangular, pentagonal and hexagonal prisms. Adding to them a heptagonal prism, we obtain all the elementary fullerenes of the Δn=2 series (Fig. 2).

Fusion of two tetrahedrons. Suppose that two tetrahedral carbon molecules react in the following manner $C_4 + C_4 \rightarrow (C_4C_4) \rightarrow C_8$. In Fig. 3 the atomic configurations corresponding to this reaction are shown. At first two molecules C_4 are moving towards each other (Fig. 3a). Then the atoms, marked with red, interact with each other and produce a compound (Fig. 3b). During this process new covalent bonds (red lines) are formed and old covalent bonds between the reacting atoms (brown lines) are disintegrated. As a result, a nonahedron is formed (Fig. 3c) which consists of three adjacent hexagons of boat conformation (Fig. 1).

One can describe this process with the help of graph theory as it is shown in Fig. 3 below. At first we have two independent graphs (Fig. 3d), then we obtain the vertex-connected graph having eight vertices, nine stable and six unstable old edges, together with three new formed edges (Fig. 3e), and at last, the graph corresponding to three-fold symmetry of the fullerene formed is composed (Fig. 3f). It seems that analyzing the fullerene reaction in the frame of graph representation is a simpler task. Obviously that it is connected with the fact that the graph approach reduces a three-dimensional problem to a two-dimensional one.

Fusion of two triangular pyramids can be written as $C_6 + C_6 \rightarrow (C_6C_6) \rightarrow C_{12}$ and can be analyzed similar to the previous reaction. It is presented in Fig. 4 as joining two pyramids and as a connection of two graphs. The fullerene obtained can be named as a triangular barrel-shaped fullerene.

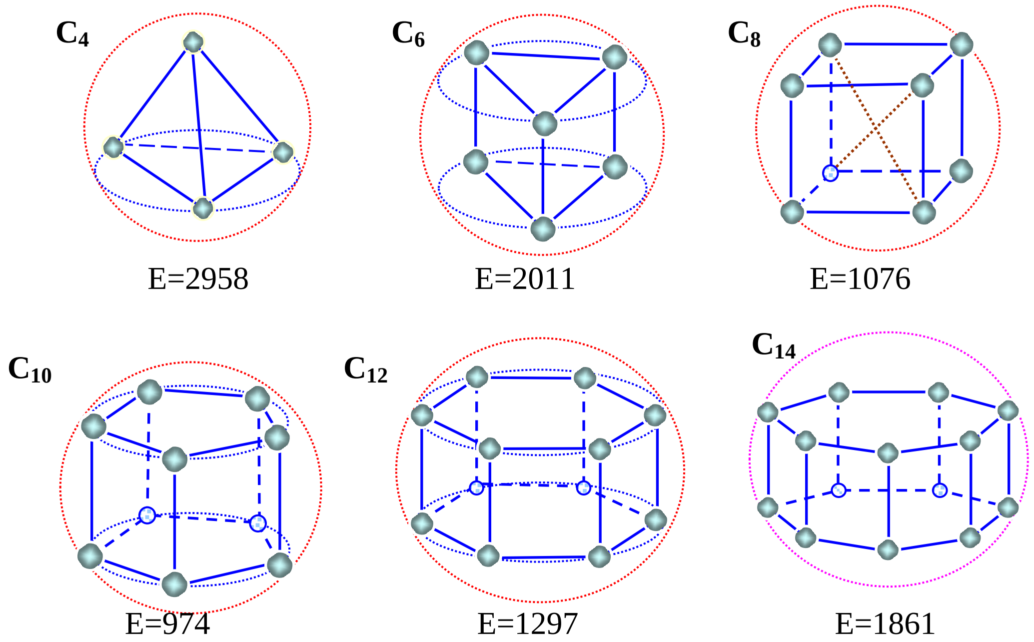

Fig. 2. Structure and energy (kJ/mol) of the Δn=2 series fullerenes with single bonds

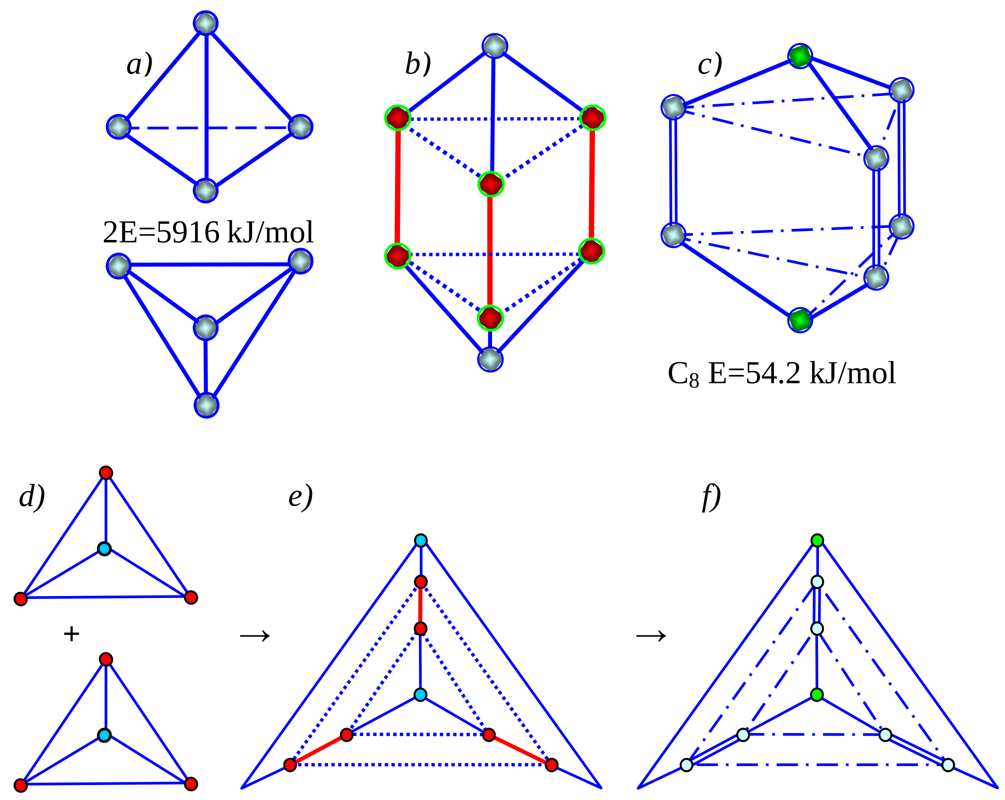

Fig. 3. Mirror-symmetry joining two tetrahedrons into a nonahedron of three-fold symmetry above and graph representation of this fusion reaction below:
a, *d*) Separate tetrahedrons; *b*, *e*) Intermediate compound; *c*, *f*) Nonahedron;
Blue and red balls are neutral and reacting atoms, respectively; green balls are neutral atoms showing a three-fold symmetry; red lines are new covalent bonds forming; blue lines are old and new covalent bonds; dot blue lines are covalent bonds to be destroyed; dash-dot blue lines are bending lines of hexagons

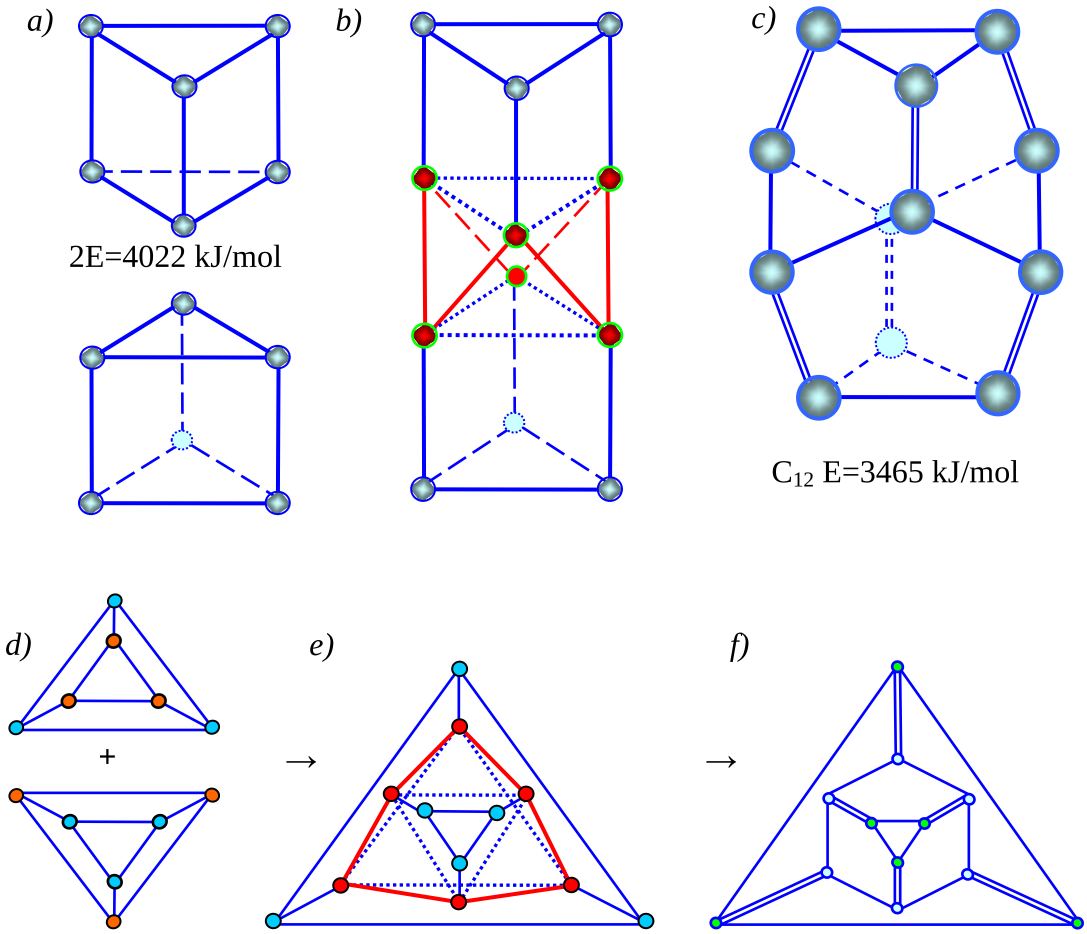

Fig. 4. Rotation-reflection-symmetry joining two triangular prisms into a triangular barrel above and graph representation of this fusion reaction below;
a, *d*) Separate prisms; *b*, *e*) Intermediate compound; *c*, *f*) Triangular barrel;
Blue and red balls are neutral and reacting atoms, respectively; green balls are neutral atoms showing a three-fold symmetry; red lines are new covalent bonds forming; blue lines are old and new covalent bonds; dot blue lines are old covalent bonds to be destroyed

Fusion of two cubes. This reaction, $C_8 + C_8 \rightarrow (C_8C_8) \rightarrow C_{16}$, is illustrated in Fig. 5 as a connection of graphs, together with a fullerene obtained. One of two initial cubes is also presented in Fig. 5.

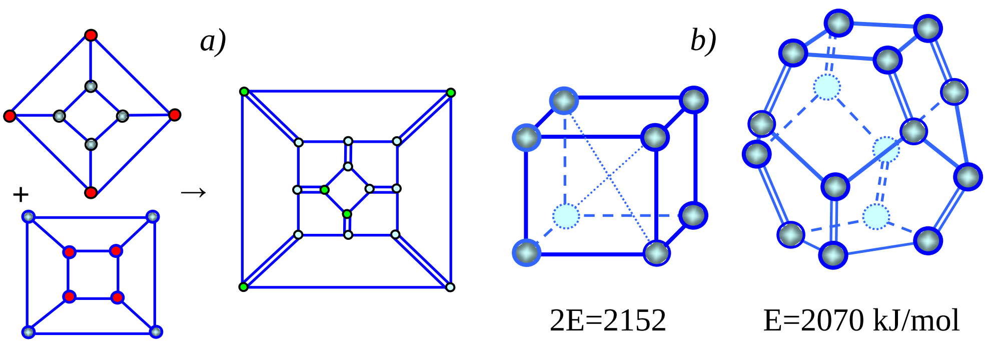

Fig. 5. Fusion of two cubes as joining their graphs (*a*);
cubic fullerene C_8 and square barrel-shape fullerene C_{16} (*b*)

Fusion of two pentagonal prisms is written as $C_{10}+C_{10}\to(C_{10}C_{10})\to C_{20}$. It is shown both as a graph connection and as an initial and a final geometric body in Fig. 6.

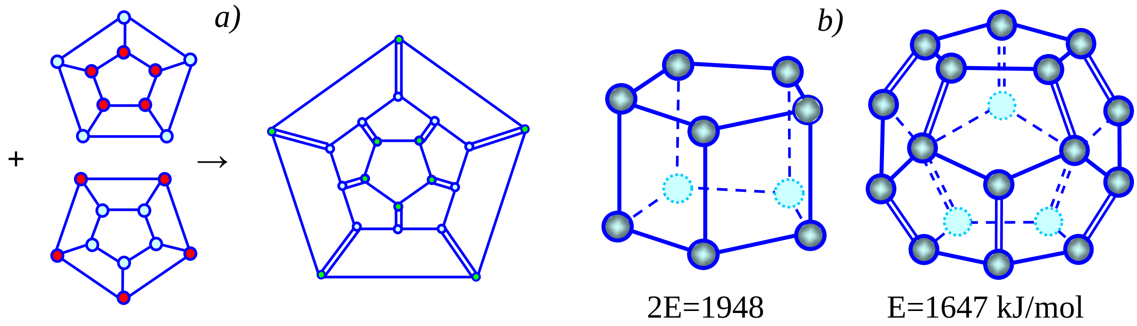

Fig. 6. Fusion of two pentagonal prisms as joining their graphs (*a*); pentagonal prism C_{10} and five-cornered barrel-shape fullerene (dodecahedron) C_{20} *(b)*

Fusion of two hexagonal prisms, written as $C_{12}+C_{12}\to(C_{12}C_{12})\to C_{24}$, is displayed both as a graph connection and as an initial and a final geometric body in Fig. 7.

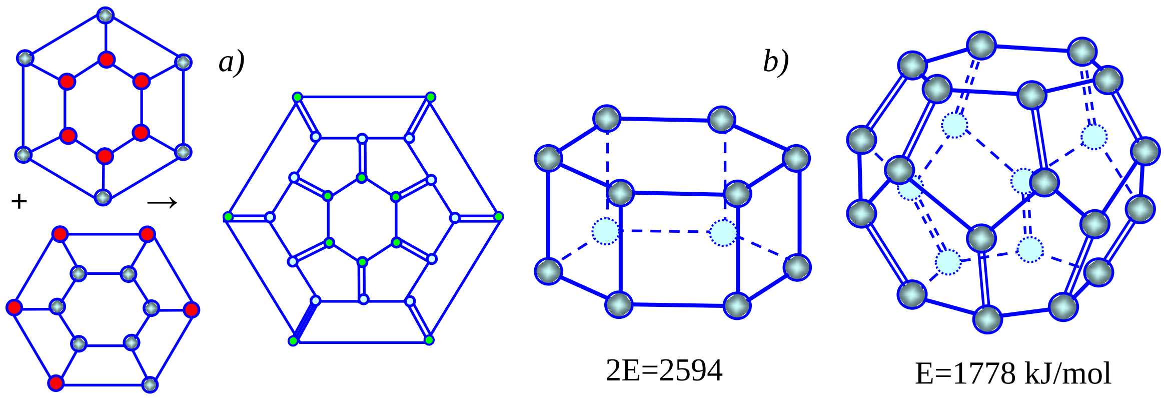

Fig. 7. Fusion of two hexagonal prisms as joining their graphs (*a*); hexagonal prism C_{12} and six-cornered barrel-shape fullerene C_{24} (*b*)

Fusion of two heptagonal prisms, $C_{12}+C_{12}\to(C_{12}C_{12})\to C_{24}$, is presented in Fig. 8 as connection of graphs, together with an initial prism and fullerene C_{28} obtained.

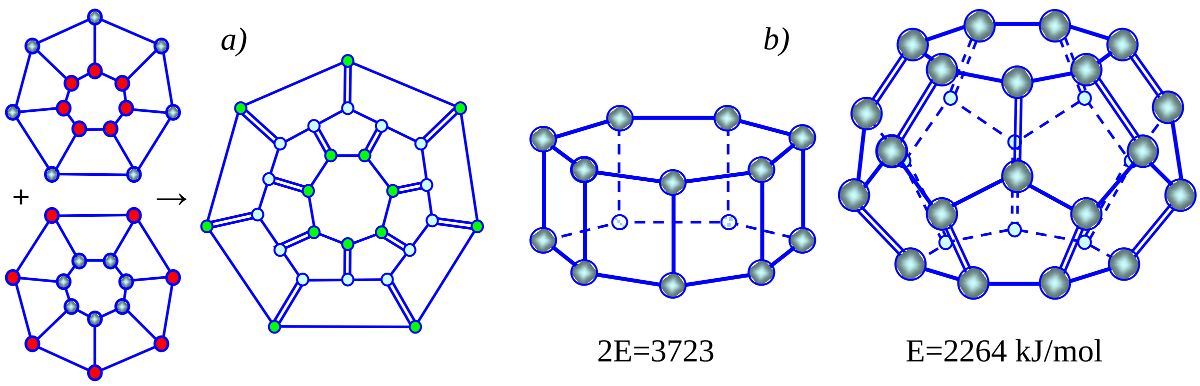

Fig. 8. Fusion of two heptagonal prisms as joining their graphs (*a*); heptagonal prism C_{14} and seven-cornered barrel-shape fullerene C_{28} *(b)*

4. Conclusion and discussion

We have considered reactions of elementary fullerenes (from C_4 to C_{14}) with each other. Under the elementary fullerenes we understand a tetrahedron, a cube, and triangular, pentagonal, hexagonal and heptagonal prisms. The process is similar to fusion of bubbles in a soap solution. The graphs describing the process are suggested. It is supposed that during the reactions new covalent bonds are formed and old covalent bonds between the reacting atoms are destroyed. The reaction zone takes into account the fact that covalent bonds exist only between nearest-neighbor atoms. The fusion reactions are exothermic. The $\Delta n=4$ series fullerenes of the periodic system of fullerenes are obtained.

There are a lot of papers on fullerene properties [7, and 277 references therein]. Using different computational methods (there are also a lot of programs), the authors calculate the properties of the most popular fullerenes which structure is known. As a result, the numbers obtained contradict to each other and only increase disordered information. To our mind, the absence of appreciable progress in understanding fullerene nature is determined by the domination of numerical calculations on the known structures. Consequently, it is necessary not to do various calculations only on the known structures which are poorly connected with each other, but to study simultaneously the definite series or columns of the fullerene periodic system suggested [1, 2].

Therefore, the next reasonable step in investigation is obtaining the structure and energy of missing fullerenes with the purpose to incorporate the missing known and unknown fullerenes in the periodic system. Only afterwards, having a comprehensive picture, it seems wise to explain why some fullerenes are more stable than others.

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